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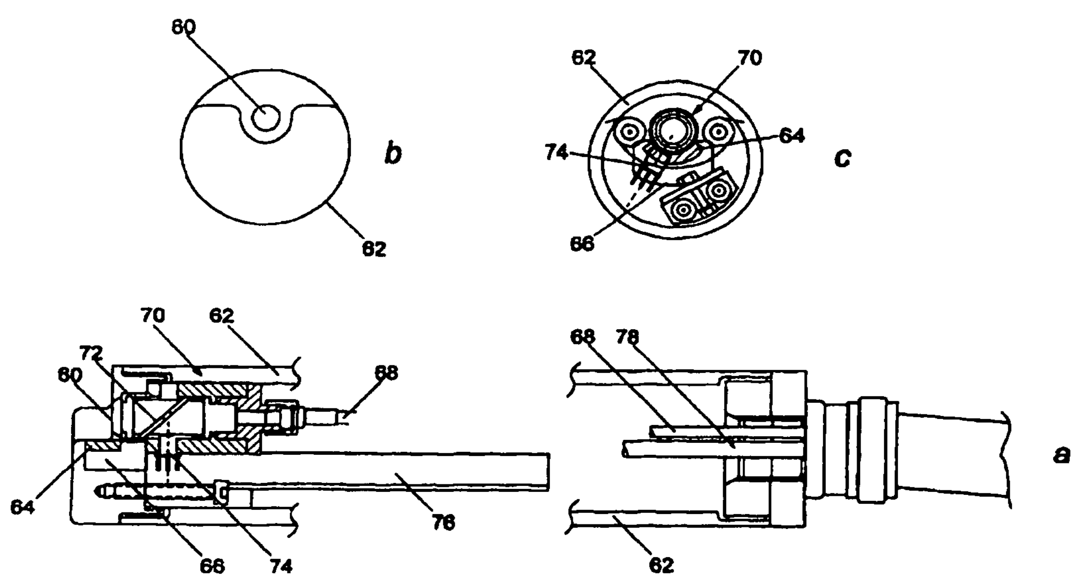

(57) Abstract

A sensor has a cylindrical body (62) the front of which can be inserted in a body of liquid. Laser pulses are coupled via a fibre optic cable (68) and optical assembly (70) to enter the liquid via a window (60). Interaction of the laser energy with an analyte of interest produces acoustic waves in the region adjacent the window (60) which are detected by an acoustic transducer (64). Preferred forms of transducer and their mounting are disclosed.

"Measurement Sensor and Method"

This invention relates to the use of a combined optical and acoustic technique for the detection and measurement of selected analytes in fluids.

It is well known to use techniques in which a pulse of laser light is directed into a liquid, the wavelength of the light being such that it is absorbed by the selected analyte or combinations os analytes and base material, and such absorption generates a transient pressure pulse which can be detected and measured by a suitable pressure sensor, typically a piezoelectric element. The general technique is described, for example, in "Theory of the pulsed optoacoustic technique", H M Lai and K Young, J. Acoust. Soc. Am. 72 (6) 2000-2007 (1982).

Although it is known that such techniques can provide a sensitive analysis of low concentrations of analytes, their use has hitherto largely been restricted to the laboratory and they have not been in common use in industrial situations.

According to the present invention there is provided a sensor for measuring the concentration of one or more selected analytes within a body of fluid, the sensor comprising a housing adapted to be positioned directly in or near the surface of a body of fluid; light transmission means for receiving light pulses from a laser source; lens means carried by the housing and

having optical components to direct the light with a desired geometry and form from the light transmission means to a target location outside the housing, the target location in use being within the body of fluid; acoustic transducer means mounted on the housing so as to be positioned, in use, in the vicinity of said target location; and electric signal means coupling the output of the transducer means to display and/or data processing means remote from the housing.

Preferably, the transducer means is positioned, in use, within said body of fluid.

The body of fluid may be a stationary body, such as the liquid within a tank or a borehole, or may be a fluid stream such as a liquid flowing within a pipe.

In one form of the invention, the housing is of generally cylindrical form and has a front end which forms an open measurement region which, in use, is introduced into a pipeline via a circular port. This is particularly useful in measuring and monitoring applications in an industrial environment, one example being the measurement of small proportions of hydrocarbons in process or produced water, other outfalls and discharges and groundwater.

The lens means may comprise a lens assembly within the housing operating in conjunction with a fluid-tight optically transmissive window in the housing. Alternatively, a graded (or gradient) refractive index lens may be used, and this may itself form a window in the housing.

The transducer means may suitably be carried on an extension projecting from the front end of the housing.

In one form, the transducer means comprises an element of piezoelectric material (for example, a disc-shaped crystal of lead zirconate titanate or the like) with the disc axis aligned perpendicularly to the optical axis. Preferably, however, the transducer means comprises one or more piezoelectric elements shaped, ideally, to match the wavefront of the acoustic pulse; for example by presenting one or more part-cylindrical surfaces disposed around the optical axis.

The piezoelectric element(s) preferably have a thickness which is substantially equal to the product of the duration of the compressive part of the acoustic impulse and the velocity of sound in the piezoelectric material.

An important preferred feature of the invention resides in the provision of damping mass to prevent or reduce ringing of the transducer crystal(s). Preferably, the damping mass is in the form of a volume of lead or other suitable material secured to the rear face of the or each crystal and shaped to inhibit the generation of acoustic resonances.

From another aspect, the invention provides a method of measuring the concentration of one or more selected analytes within a body of fluid, the method comprising forming pulses of laser light of an optical frequency absorbed by the selected analyte(s), coupling the light pulses into a body of fluid to be focused at a target location within the body of fluid, detecting acoustic pressure pulses at a location adjacent said target location, and analysing the resultant signals to determine the relative concentration of the selected analyte(s).

The body of fluid may be a stationary body, or a flowing stream.

Preferably, said pulses have a pulse duration which is shorter than the time required for thermal diffusion across the diameter of the optical interaction region. In general terms, this could be in the range 1ns to less than 1μs. In the embodiments discussed herein, the pulse length will typically be in the range 5 - 200ns, most preferably 50 - 75ns.

A particular application of the method is in detecting the presence of hydrocarbons in water, in which case the light pulses may suitably have a vacuum wavelength of 600 to 3500nm.

The analysis of the acoustic signal may suitably be carried out on values averaged over a number (suitably up to 10,000, and typically between 100 and 5000) of discrete signal samples.

The analysis may simply be a peak-to-peak measurement, or may include examination of the rise and fall times of the acoustic waveform, or may be based on a Fourier analysis of the waveform, and other temporal properties of the acoustic response.

Alternatively, the analysis may be based on integration of the acoustic waveform to obtain an energy-related signal.

The present invention further provides an acoustic sensor comprising means for emitting pulses of light of selected wavelength to produce acoustic pulses in a fluid, and a pressure sensitive element for detecting said acoustic pulses, the pressure sensitive element

having a rear face against which is secured a backing element to provide both inertial loading and vibrational damping.

Typically, the pressure sensitive element is a piezoelectric ceramic crystal, for example of lead zirconate titanate, or other piezoelectric material and the backing element is of lead.

The backing element is preferably configured to minimise acoustic reflections, as by being formed with non-parallel surfaces, or by any surfaces which are parallel being formed with discontinuities.

Embodiments of the present invention will now be described, by way of example, with reference to the accompanying drawings, in which:

Fig. 1 is a schematic cross-sectional side view of one embodiment of photoacoustic detector instrument in accordance with the invention;
Fig. 2a is a cross-sectional side view showing part of a second embodiment;
Fig. 2b is an end view of the detector of Fig. 2a:
Fig. 3a is a cross-sectional side view of a third embodiment;
Fig. 3b is an end view of the detector of Fig. 3a;
Fig. 3c is a cross-section on C-C of Fig. 3a;
Fig. 4 is a cross-sectional side view of a further embodiment of photoacoustic detector instrument;
Fig. 5 is a graph illustrating waveforms generated in use of the system.

Referring to Fig. 1, a detector instrument comprises a generally cylindrical fluid-tight housing 10 formed from two cylindrical members 12 and 14 joined together

at flanges 16 and 18. In use, the forward cylindrical member 12 is inserted into a pipeline (not shown) through a conventional ball valve and muff coupling (not shown) with O-rings or other sealing elements and provision for clamping and safety interlocks.

Light from a laser source is coupled to the instrument via a fibre optic system 20 to a launching unit 22. The launching unit 22 produces a beam which passes via a fluid-tight window 24 into fluid flowing within the pipeline.

An acoustic sensor 26 is located adjacent the window 24 in an extension 28 projecting from the housing 10. The sensor 26 suitably comprises a disc of a piezoelectric ceramic material and is backed by a lead cylinder 30 secured within the extension 28 by a plug 32.

The lead cylinder 30 acts to damp ringing of the PZT crystal and to better perform this function is preferably bonded to the crystal 26, for example by electrically conductive epoxy which acts as an electrical connection to the rear face of the crystal 26, from which the piezoelectric signal is obtained. The connection to the front face of the crystal 26 is achieved with wrap-around electrodes which permit contact wires to be bonded via the side of the crystal 26.

It will be appreciated that laser light pulses emerge from the optical assembly in the vicinity of the end of the instrument adjacent the crystal 26. Resulting photoacoustic pressure pulses are detected by the crystal 26 to form analog electrical signals representative of the transient pressure amplitude. The suppression of ringing by the lead backing enables

the crystal 26 to operate as a broad band transducer without unduly reducing its sensitivity.

The electrical output from the crystal 26 is coupled to amplifying electronics mounted on a printed circuit board 34 within the housing 10, to provide output signals via electrical connections 36.

The optical pulse has an energy of the order of typically a micro-Joule, and generates a low energy photoacoustic signal which propagates radially from the optic axis with a particular acoustic wavefront geometry which depends on the absorption of the analyte and the optical beam geometry.

Fig. 2 illustrates a modified instrument in which it is sought to improve the interaction between the photoacoustic pulse and the sensor.

In Fig. 2, once again the instrument is of basically cylindrical form for insertion into a pipeline, and laser light pulses from a fibre optic cable and focusing lens assembly (not seen in the Fig) are transmitted via a window 40 into liquid flowing within the pipeline.

In this embodiment, the detector comprises a pair of piezoelectric crystals 42 and 44 (suitably of lead zirconate titanate) each of part-tubular shape arranged within part-cylindrical housings 46, 48 forming projections from the main cylindrical housing 50 of the instrument. The housings 46, 48 define between them a passage 52 for flow of liquid within which the photoacoustic interaction occurs. The shape and disposition of the crystals 42, 44 is chosen to maximise the area available for reception of the

photoacoustic pulse, to keep the angle of incidence of the acoustic wavefront on the crystal within acceptable limits, and also to minimise timing differences in the pressure wavefront reaching the crystal.

Each of the crystals 42, 44 is once again provided with damping, in the form of lead backing pieces 54, 56 of complementary shape.

This embodiment gives improved coupling between the photoacoustic wave and the piezoelectric material for the optical geometry utilised. However, the construction is relatively complex, and the channel 52 is relatively restricted.

Fig. 3 shows a presently preferred embodiment. This follows similar principles to Fig. 2, but has a window 60 displaced from the centre line of housing 62, and a single transducer crystal 64 of part-cylindrical shape backed by a lead body 66. The liquid in the vicinity of the instrument is therefore not restricted to a channel, but the coupling efficiency approaches that of Fig. 2.

In the embodiment of Fig. 3, laser pulses are coupled via a fibre optic cable 68 to a lens assembly 70 which includes a beam splitter 72. The beam splitter 72 diverts a known proportion of the laser energy to a photosensitive detector such as a photodiode 74. This permits the applied laser energy to be monitored, and the detected acoustic signal can be normalised in relation to the applied optical energy.

The housing 62 is suitably of 38mm diameter in stainless steel, and contains an electronics module 76 which communicates with a remote processing and display

circuit via a multi-way cable 78. The cable 78 may use a combination of fibre optic signal paths and low voltage, low power electrics for intrinsically safe operation in hazardous locations.

Fig. 4 shows another approach in which a sensor 100 of generally cylindrical form projects into a flow channel (not shown). The sensor body has a cylindrical passage 102 transverse to the main axis of the body, and thus aligned with the fluid flow, the passage 102 containing an insert 104 shaped to define a venturi.

An optical fibre cable 106 delivers laser light to a GRIN (graded refractive index) lens 110 located at the venturi throat. At the opposite side of the throat, a passage 112 communicates with a tubular conduit 114 whose other end is open to the fluid flow passage.

Thus, in use, fluid flow through the venturi causes a reduction in pressure at the venturi throat which draws fluid through the conduit 114.

An ultrasonic transducer is provided in the form of a lead zirconate titanate tube 108 which is backed by a lead mass 116 and butted against an insulating pad 118 and solid end cap 120. The lead mass 116 has the shape of a hollow tapered cylinder, the shape being chosen for effective damping.

This embodiment has the advantage of using a complete cylinder of piezoelectric material, and thus achieving higher sensitivity and coupling for the optical geometry utilised.

Similar considerations apply to the operation of all the foregoing sensor assemblies, as will now be

discussed.

The piezoelectric element should be dimensioned to give an optimum response to the generated acoustic wave. Ideally, the thickness corresponds to the equivalent distance travelled by the compressive part of the acoustic impulse in the particular piezoelectric material; that is, the product of the duration of the compressive part and the velocity of sound in the piezoelectric material.

The efficiency of operation is maintained by installing the piezoelectric element behind a thin layer of stainless steel, preferably 0.1mm in thickness although thicker layers are possible. An example is illustrated at 150 in Fig. 4.

The backing or damping material with appropriate acoustic impedance matching to the piezoelectric element(s) should minimise the formation of back reflections or standing waves from the incident acoustic wave, and also damp the natural acoustic resonances of the piezoelectric crystal. This can be approached by using a shape which has a minimum of parallel surfaces, for example as in the shapes of lead backings shown in Figs. 3 and 4. Alternatively, if parallel surfaces occur, additional features such as conical holes may be introduced to disrupt the formation of acoustic resonances.

A further preferred feature of the invention is the use of very short pulses of laser light. The object is to choose a pulse length which is shorter than the time required for diffusion of thermal energy in the region of interaction in the medium concerned, in order that the process of energy conversion occurs in a very

localised way within the optical interaction region. This very rapid heating results in an acoustic impulse which has a distinctive compression followed by a rarefaction without significant bulk thermal expansion taking place. In this regime, the frequency content of the waveform may be used to characterise the components of the system under examination.

A suitable pulse length, depending on the substances and frequencies involved, may be between 1ns and 1μs. Typically, a pulse length of 10 - 200ns will be suitable, and most commonly 50 - 75ns is preferred for best results.

A further advantage of an ultrashort pulse regime is that the range of frequencies within the acoustic wave is in the ultrasound region, and thus the sensor is substantially immune to the effects of normal mechanical vibration and the effects of turbulence in flowing liquids. In this regime the acoustic signal is also substantially immune to the effects of optical scattering. An additional advantage is that the transient response can be used to characterise the component analytes in the system.

The choice of laser system to be used will be determined by the analyte(s) under consideration, and may take the form of a set of diode lasers, or a solid state tunable laser such as a Neodymium YAG laser with an optical parametric oscillator (OPO). For the particular application of the monitoring of hydrocarbons in water, the laser source may be a diode laser operating in the near infrared spectral range at wavelengths between 600 and 2500nm. In this form, the invention makes it possible to measure low (ppm) concentrations of hydrocarbons in water, but it can

also be optimised for medium (1%) concentrations and high (up to 100%) concentrations.

The exact choice of laser wavelength depends on the particular hydrocarbon analyte or mixture of analytes in the system. A number of laser sources at different wavelengths may be used as determined by the required measurement accuracy and the particular calibration procedure adopted. The calibration procedure may be in the form of a look-up table, a multiple regression analysis, a neural network procedure, or other statistical procedure.

It is also possible to use a tunable laser with continuous coverage from the visible to the mid infrared spectral region. This allows the full spectrum of each analyte to be obtained, which makes the sensor useful in analysis of pollutants, and in process control, in (for example) the petrochemical and food processing industries.

The laser output is coupled to a fibre optic delivery system via a suitable lens system. In the case of multiple diode lasers, a fibre optic wavelength multiplexing or other optical coupling can be used to combine the outputs of the laser sources into a single delivery fibre.

At the detector head, the optical pulse is finally delivered through a conventional lens assembly as in Fig. 1, or a GRIN lens as in Fig. 4, or other refractive or diffractive optical elements. In each case, the aim is to achieve the optimum optical beam and the optimal pulse duration, based on the optical absorption and acoustic transit time within the beam.

The end faces of the lens system used may be coated to minimise optical reflections, and/ or to increase abrasion resistance, and/or for inhibition of organic or other fouling. Alternatively, a hard transparent material such as diamond or sapphire may be used.

To inhibit fouling of the optical system, the output lens can be coupled to an additional piezoelectric element and vibrated to achieve ultrasonic cleaning of the optical element. This facility can be deployed either continuously or intermittently. In the latter case, cleaning may be initiated in response to the appearance of a small preliminary acoustic signal which has been generated at the output interface and transmitted to the main piezoelectric element via the body of the detector head.

As indicated in Fig. 1, it is preferred to use amplifying electronics within the detector head in close proximity to the piezoelectric element. A suitable arrangement is for the electric signal from the piezoelectric element to be amplified by a voltage or charge pre-amplifier, further amplified in a programmable gain amplifier, and then digitised by an analog-to-digital converter, the digitised signal then being transmitted to a location remote from the detector head for further processing. Suitably, the detector head is connected to the remote location by a flexible umbilical containing both electrical signal paths and optical fibres.

The detector head may also be provided with means for monitoring the laser pulse energy, to permit the acoustic signal to be normalised to the value of the optical pulse energy. The optical energy may be measured at the point where the diode laser is coupled

to the optical fibre, or at the detector head, for example by diverting a small proportion of the light from the main fibre optic path to a photosensitive detector, as in Fig. 3. Alternatively, an interfacial reflection at the fibre output end may be utilised for this purpose via detection at the input end.

A suitable form of processing is to average the digital signal over a number of samples, which may be up to 10,000 (typically between and 100 and 5000) depending on application. The value of the peak to peak voltage of the transducer for the acoustic pulse is then recorded for each of the wavelengths of operation, and divided by the amplitude of a signal which relates to the input energy, for normalisation and comparison with calibration data. Either the full wave form or the peak to peak values can be stored for later analysis.

Calibration of the system may be carried out through standard routines of comparison, linear regression, multivariate analysis, or a neural network system.

However, the signal analysis may alternatively be based on analysis of the inherent temporal information contained in the acoustic signal.

Referring to Fig. 5, the optical pulse 160 results in an acoustic pulse 162 being generated, the acoustic pulse 162 comprising a compressive pulse followed by a rarefaction pulse. One aspect of using the temporal information is to use the time delay T1 between initiation of the optical pulse 160 and the receipt of the acoustic pulse 162 to determine the velocity of sound in the fluid medium. Subsequently, the detail of the rise time T2 of the compressive acoustic wave contains information of the way that the different

analytes take up the optical energy.

Alternatively, the complete waveform can be analysed on a temporal basis. This can be interpreted either directly by measurement of rise and fall times, or via a Fourier analysis to ascertain the characteristic frequencies contained within the waveform and relate them to concentrations of particular analytes.

A further possibility is to integrate the total area of the average acoustic waveform to obtain a measure of the energy absorption dissipated as thermal energy by the analyte of interest.

Although described above with particular reference to measurement of fluids flowing within pipes and the like, the invention is not limited to such applications. For example, the same principles can be applied to monitoring industrial outfalls, measuring concentration of alcohol in water (for example in the control of distillation), and the investigation of boreholes.

Pressure sensors other than piezoelectric crystals may be used, for example piezoelectric polymers such as PVDF, or semiconductor pressure sensors which may be independent or may be part of an integrated semiconductor circuit, or optical methods including fibre optic interferometers.

Other modifications and improvements may be made within the scope of the present invention.

CLAIMS

1. A sensor for measuring the concentration of one or more selected analytes within a body of fluid, the sensor comprising a housing adapted to be positioned directly in, or near the surface of, a body of fluid; light transmission means for receiving light pulses from a laser source; lens means carried by the housing and having optical components to direct the light with a desired geometry and form from the light transmission means to a target location outside the housing, the target location in use being within the body of fluid; acoustic transducer means mounted on the housing so as to be positioned, in use, in the vicinity of said target location; and electric signal means coupling the output of the transducer means to display and/or data processing means remote from the housing.

2. A sensor according to claim 1, in which the transducer means is arranged such that, in use, it is positioned within said body of fluid.

3. A sensor according to claim 2, in which the housing is of generally cylindrical form and has a front end which forms an open measurement region which, in use, is introduced into a pipeline via a circular port.

4. A sensor according to any preceding claim, in which the lens means comprises a lens assembly within the housing operating in conjunction with a fluid-tight optically transmissive window in the housing.

5. A sensor according to any of claims 1 to 3, in which the lens means comprises a graded (or gradient) refractive index lens which itself forms a window in the housing.

6. A sensor according to any preceding claim, in which the transducer means is carried on an extension projecting from the front end of the housing.

7. A sensor according to claim 6, in which the transducer means comprises a disc-shaped or cylindrical element of piezoelectric material with its axis aligned perpendicularly to the optical axis.

8. A sensor according to claim 6, in which the transducer means comprises one or more piezoelectric elements shaped to match substantially the wavefront of the acoustic pulse.

9. A sensor according to claim 8, in which the transducer means presents one or more part-cylindrical surfaces disposed around the optical axis.

10. A sensor according to claim 9, in which the piezoelectric element(s) have a thickness which is substantially equal to the product of the duration of the compressive part of the acoustic impulse and the velocity of sound in the piezoelectric material.

11. A sensor according to any preceding claim, in which a damping mass is secured to the rear face of the or each crystal and shaped to inhibit the

generation of acoustic resonances.

12. A sensor according to claim 11, in which the damping mass is of lead or other suitable acoustically matched material.

13. A method of measuring the concentration of one or more selected analytes within a body of fluid, the method comprising forming pulses of laser light of an optical frequency absorbed by the selected analyte(s), coupling the light pulses into a body of fluid to be focused at a target location within the body of fluid, detecting acoustic pressure pulses at a location adjacent said target location, and analysing the resultant signals to determine the relative concentration of the selected analyte(s).

14. The method of claim 13, in which the body of fluid is a stationary body.

15. The method of claim 13, in which the body of fluid is a flowing stream.

16. The method of any of claims 13 to 15, in which said pulses have a pulse duration which is shorter than the time required for thermal diffusion across the diameter of the optical interaction region.

17. The method of claim 16, in which the pulse duration is in the range 1ns to 1μs.

18. The method of claim 17, in which the pulse length is in the range 5 - 200ns.

19. The method of claim 18, in which the pulse length is in the range 50 - 75ns.

20. The method of any of claims 13 to 19 for use in detecting the presence of hydrocarbons in water, and in which the light pulses have a vacuum wavelength of 600 to 3500nm.

21. The method of any of claims 13 to 20, in which the analysis of the acoustic signal is carried out on values averaged over a number of discrete signal samples.

22. The method of claim 21, in which the number of discrete signal samples is up to 10,000.

23. The method of claim 22, in which the number of discrete signal samples is between 100 and 5,000.

24. The method of any of claims 13 to 23, in which the analysis is a peak-to-peak measurement.

25. The method of any of claims 13 to 23, in which the analysis includes examination of the rise and fall times of the acoustic waveform.

26. The method of any of claims 13 to 23, in which the analysis is based on a Fourier analysis of the waveform and/or other temporal properties of the acoustic response.

27. The method of any of claims 13 to 23, in which the analysis is based on integration of the acoustic waveform to obtain an energy-related signal.

28. An acoustic sensor comprising means for emitting

pulses of light of selected wavelength to produce acoustic pulses in a fluid, and a pressure sensitive element for detecting said acoustic pulses, the pressure sensitive element having a rear face against which is secured a backing element to provide both inertial loading and vibrational damping.

29. An acoustic sensor according to claim 28, in which the pressure sensitive element is a piezoelectric crystal and the backing element is of lead.

30. An acoustic sensor according to claim 29, in which the piezoelectric crystal is of Lead Zirconate Titanate (PZT).

31. An acoustic sensor according to any of claims 28 to 30, in which the backing element is configured to minimise acoustic reflections.

32. An acoustic sensor according to claim 31, in which the backing element is formed with non-parallel surfaces.

33. An acoustic sensor according to claim 31, in which any surfaces of the backing element which are parallel are formed with discontinuities.

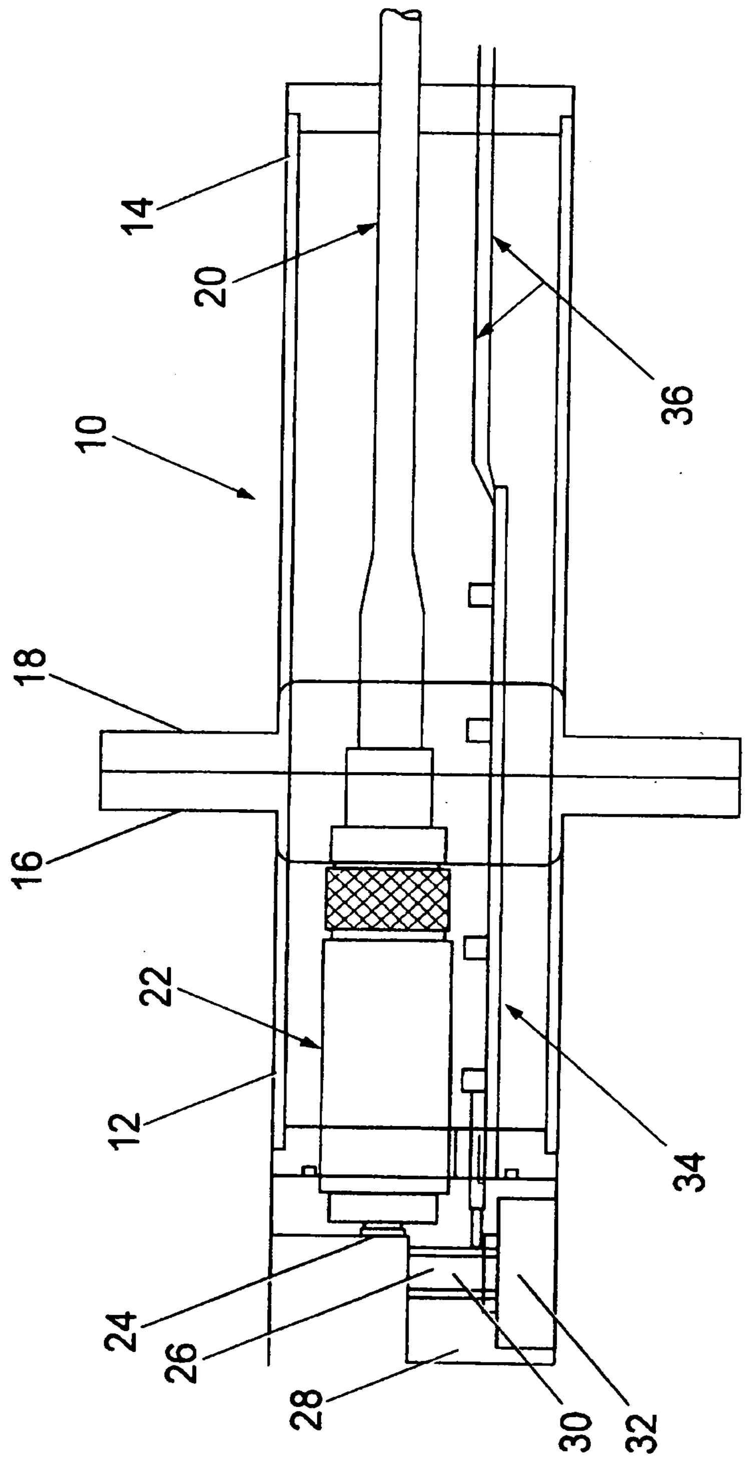

Fig. 1

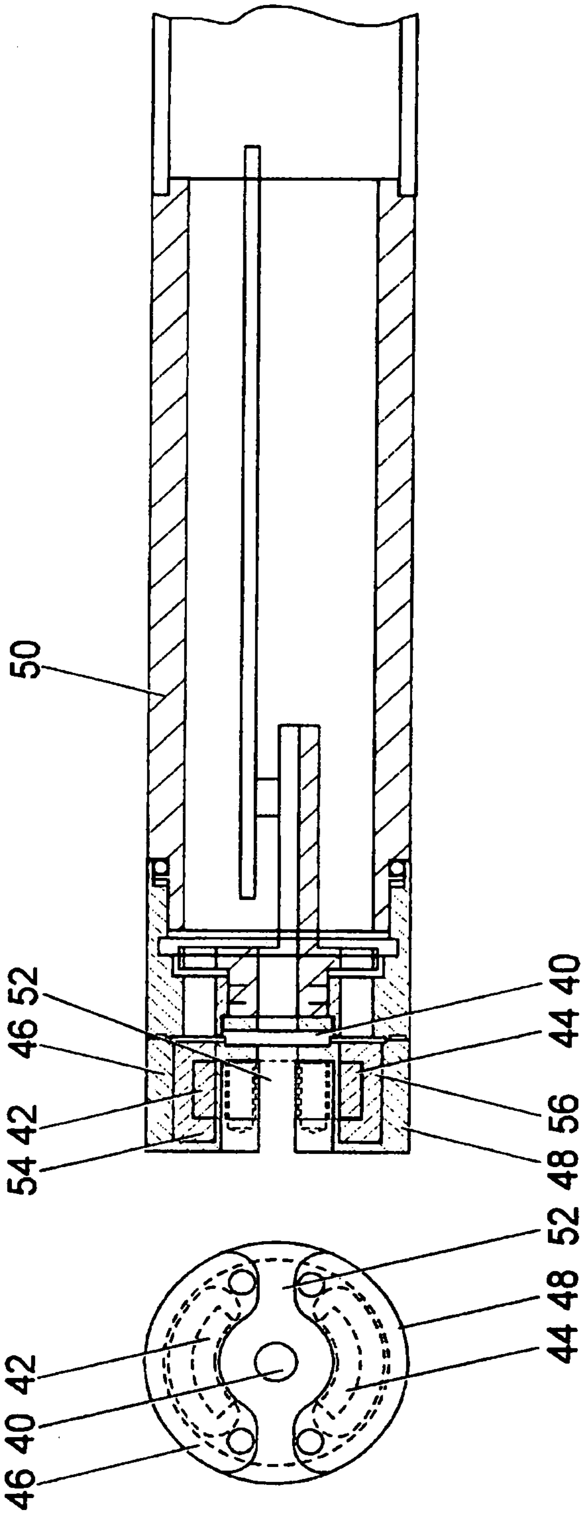

Fig. 2a

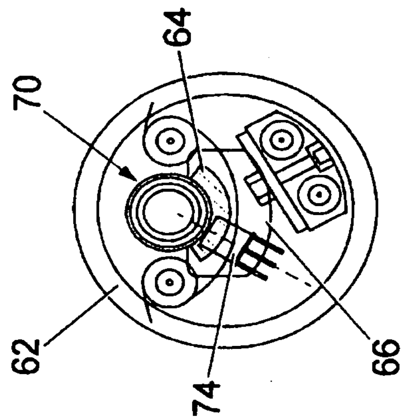

Fig. 3c

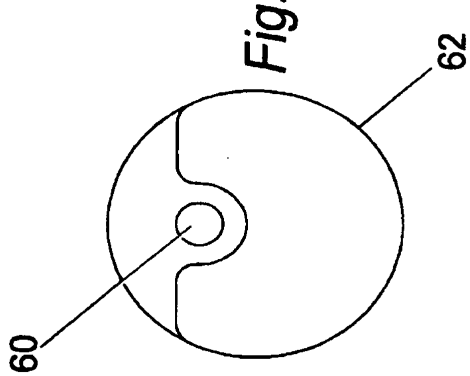

Fig. 3b

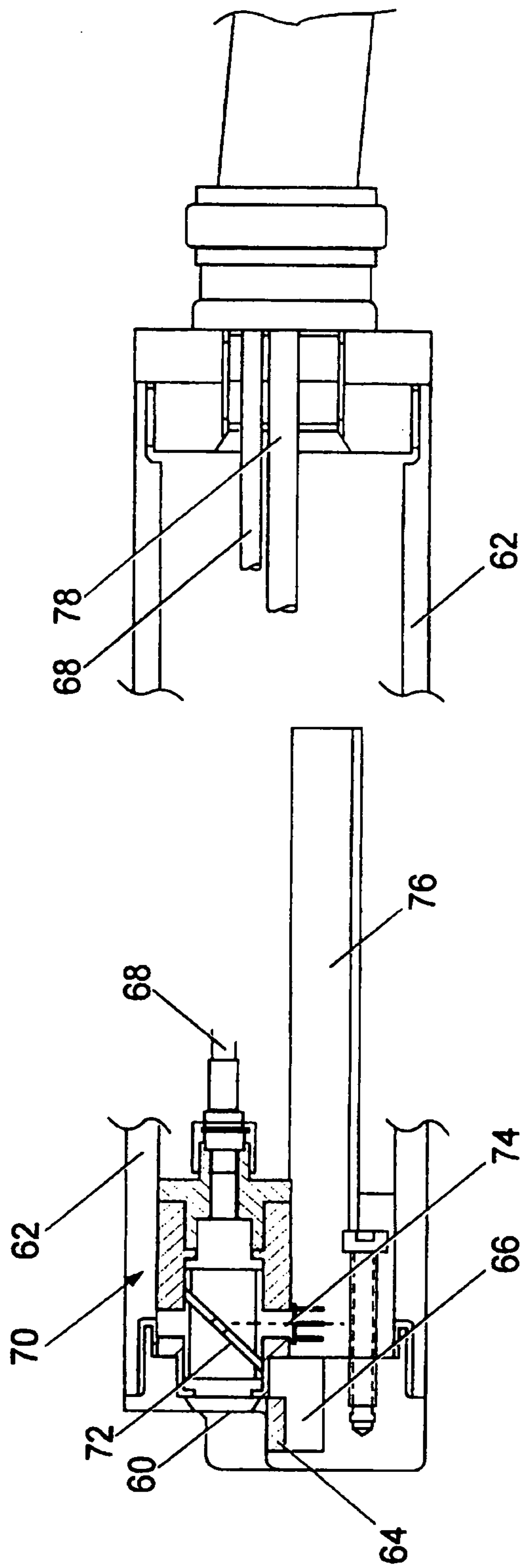

Fig. 3a

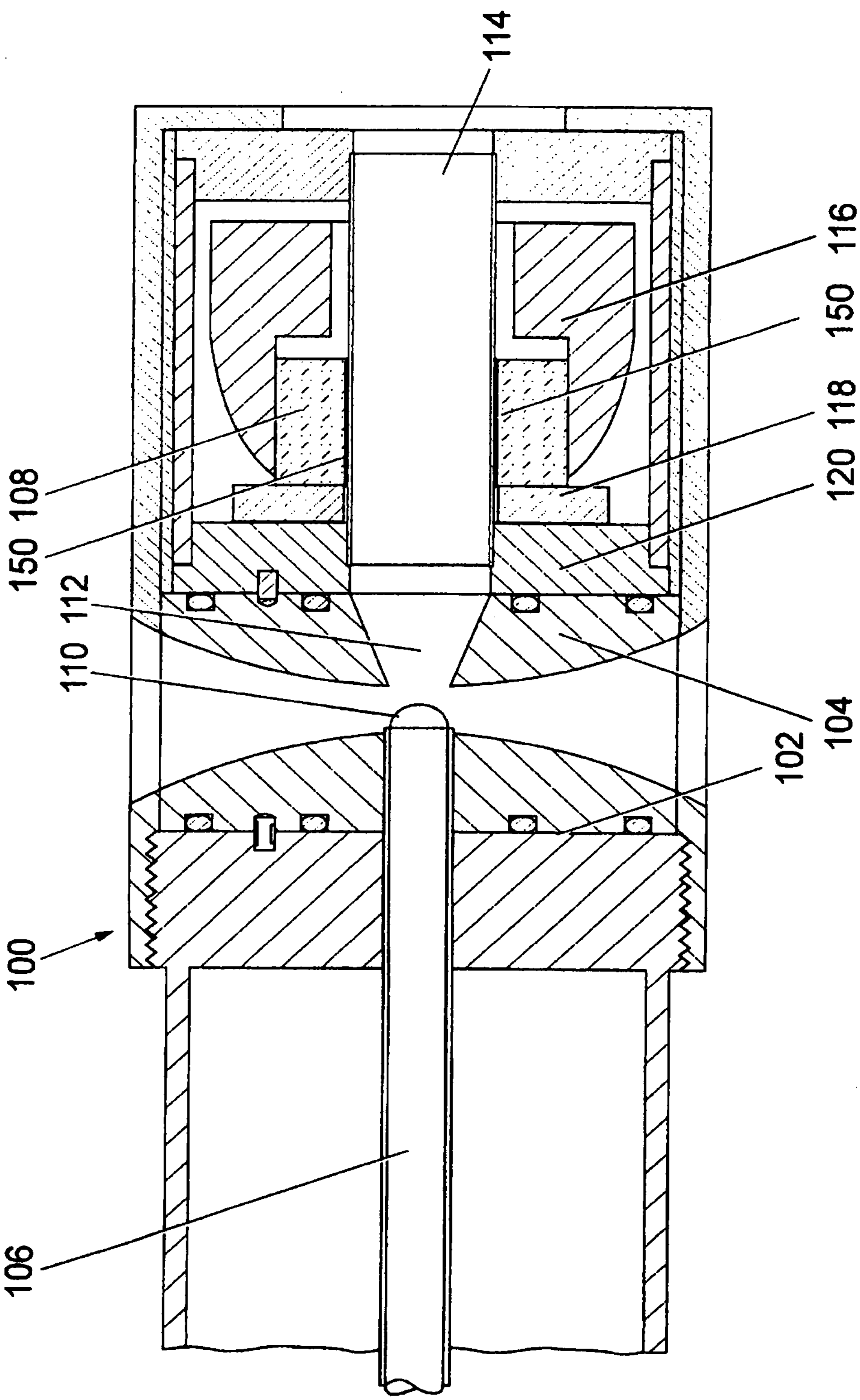

Fig. 4

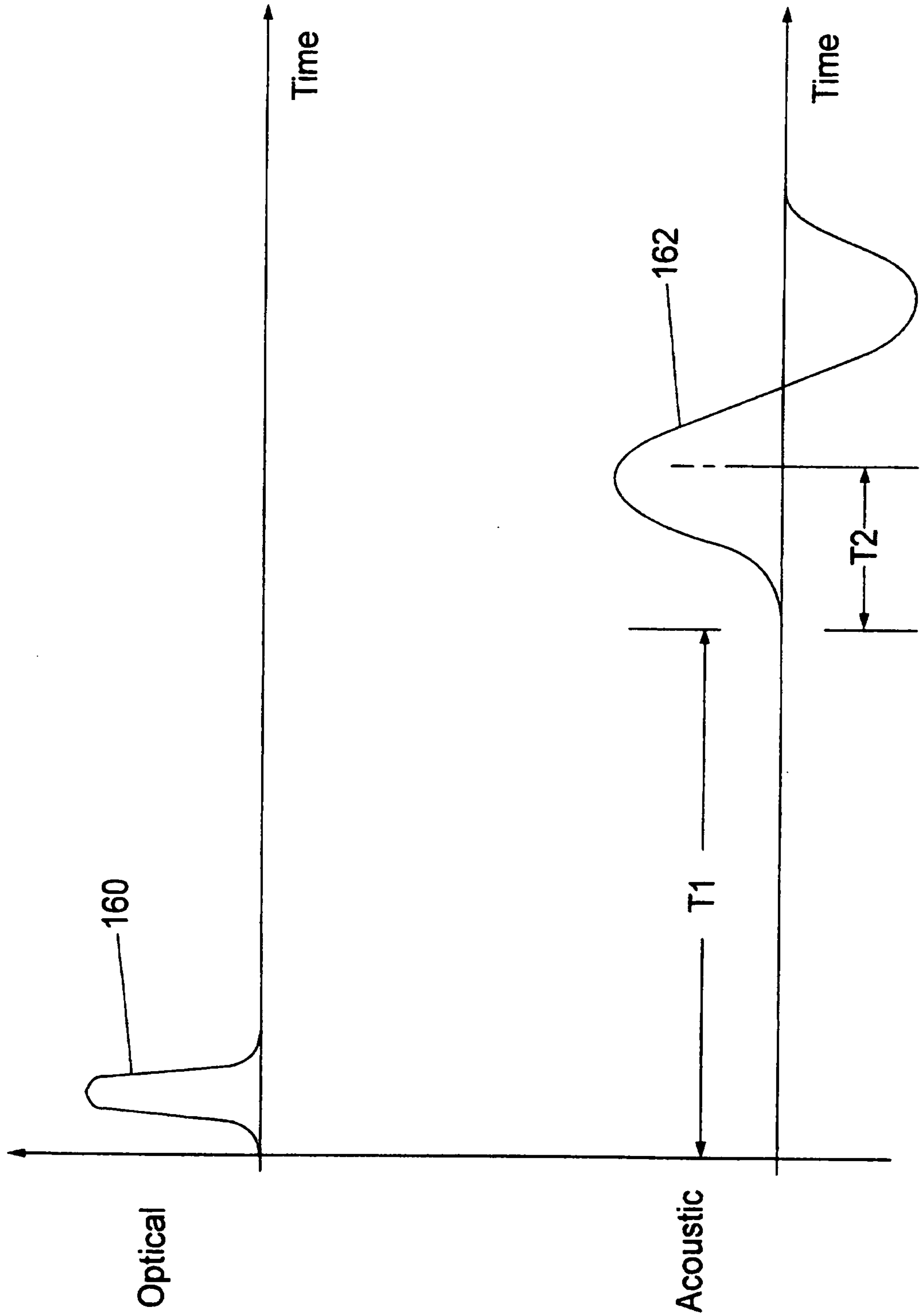

Fig. 5

INTERNATIONAL SEARCH REPORT

Internal Application No
PCT/GB 97/01890

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 G01N21/17

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 G01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 478 410 A (DOW CHEMICAL CO) 1 April 1992	1-4,6-9, 11-15, 28,29
Y	see the whole document	16-23, 26,27, 30,31

Y	US 4 303 343 A (PATEL CHANDRA K N ET AL) 1 December 1981	16,31
A	see column 3, line 53 - column 4, line 5 see column 7, line 19 - line 33; figures 2,4,5	13,28

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance
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1

Date of the actual completion of the international search	Date of mailing of the international search report
14 October 1997	12. 11. 97

Name and mailing address of the ISA	Authorized officer
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Form PCT/ISA/210 (second sheet) (July 1992)

Internat al Application No
PCT/GB 97/01890

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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